Formic Acid Partitioning at the CalNex Ground Site

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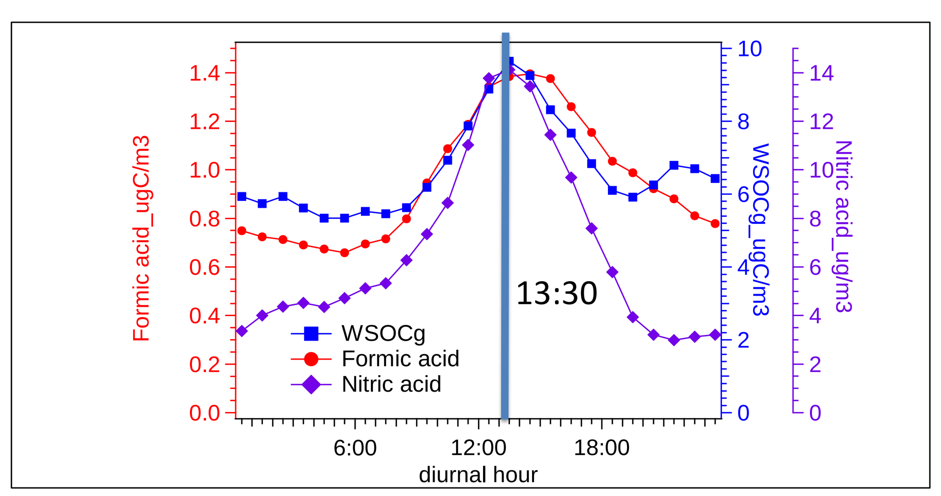
Introduction

- Formic acid is an abundant gas phase carboxylic acid (Anderson et al., Atmos.Environ., 2008); however, the partitioning of formic acid has not been extensively studied.
- During CalNex ground campaign, semi-continuous measurements of gas and fine particle formic acid and other organic and inorganic compounds were measured. These time-resolved data are used to investigate formic acid partitioning.

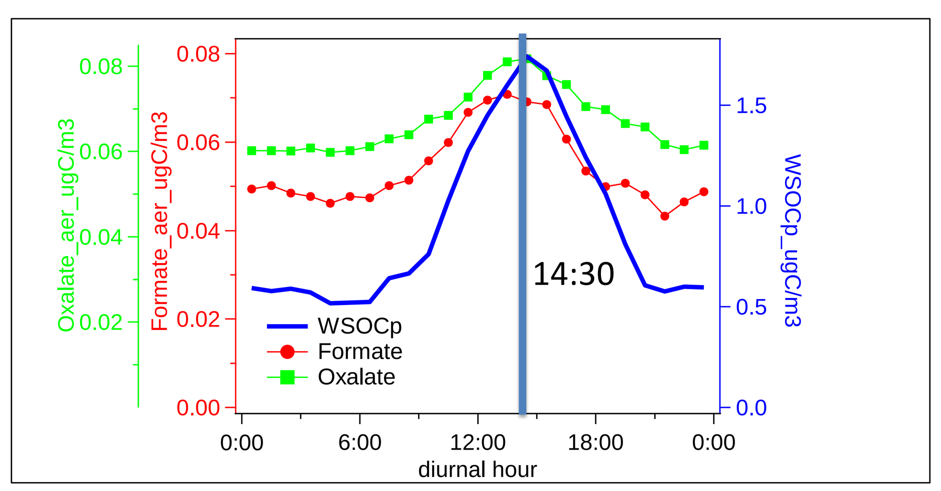
Measurements:
Gases: HNO_3 and formic acid by CIMS, WSOCg by mist chamber-TOC
Particles: PM2.5 WSOCp, oxalate, formate, nitrate by PILS, PM1 semi-volatile nitrate by AMS
Site: Caltech 5/15/2010 – 6/15/2010

Approach:
1) Investigate formic acid partitioning to water, use nitric acid partitioning to provide particle pH.
2) Investigate partitioning during low RH and highest formic acid concentrations.

General Characteristics: Gas and Particle Species

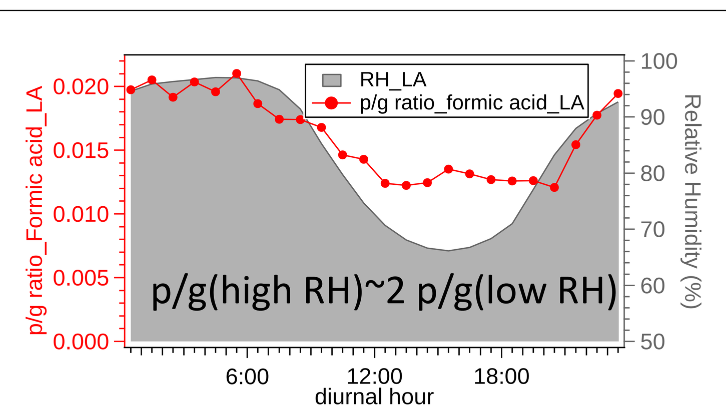


- **Gas phase:** WSOCg, formic and nitric acid: peak at same time(13:30) →photochemical production

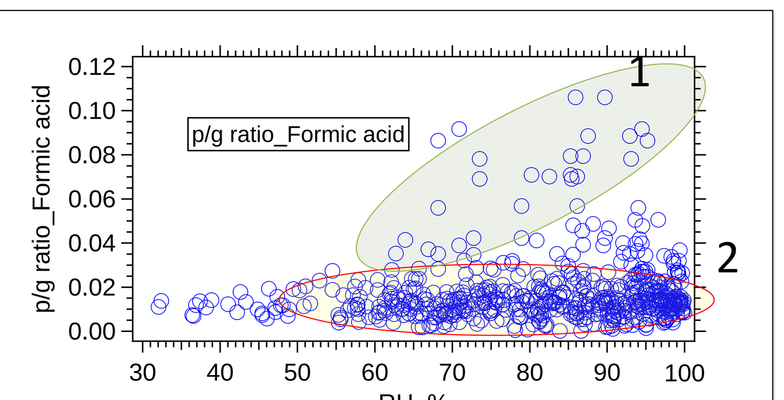


- **Particle phase:**
- Oxalate, WSOCp (e.g., SOA): peak at 14:30
- Formate: peaks earlier at 13:30, not like most SOA.

Formic Acid Partitioning: Sometimes Related to RH but Often Not



- Diurnal: Formic partitioning follows RH
- Average p/g ratio at lower RH = 1%, at high RH =2%, in range with previous studies (Chebbi et al., Atmos. Environ., 1996; Loflund et al., Atmos. Environ., 2000)

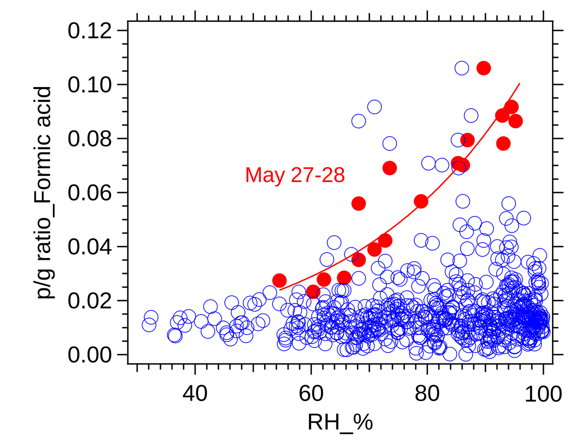


- Higher RH does not always lead to higher p/g
- Two sub-datasets for further investigation.

1. Formic Acid Partitioning to Liquid Water

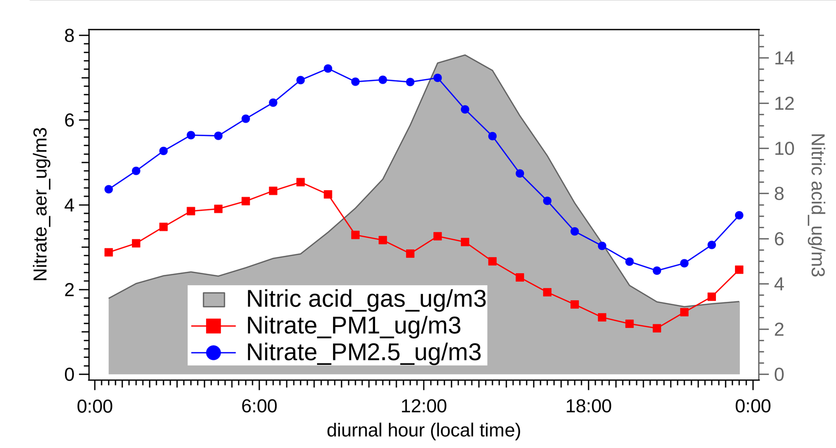
Henry's Law

$$\frac{[HCOO^-]_p}{[HCOOH]_g} = K_H * LWC * K_a * \frac{1}{[H^+]} \quad \text{Eq. 1}$$



- Eg period: May 27-28, formic acid shows partitioning to liquid water
- Assume thermodynamic equilibrium, use Henry's Law
- Use HNO3 partitioning to determine LWC/[H+] (cations not measured during study).

Nitric Acid Partitioning: Thermodynamic Equilibrium

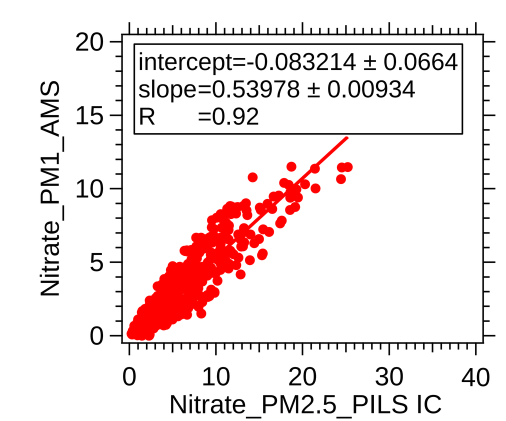


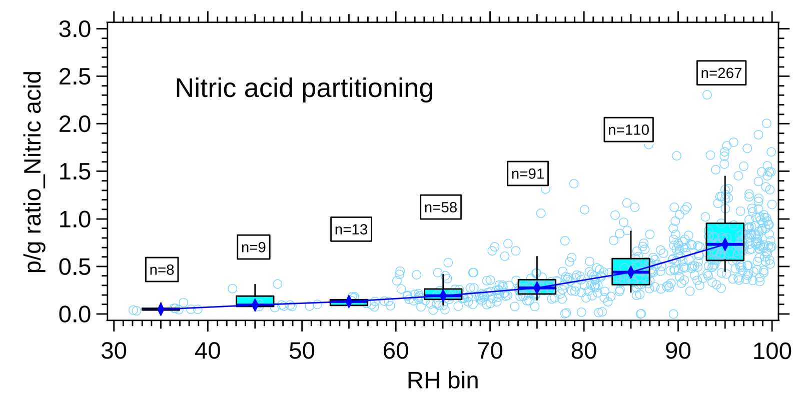
- HNO_3(g): highest concentration 13:30, same as formic acid and other SVOCs (photochemical).
- Particle phase nitrate: peak concentration in the early morning, AMS vs. PILS nitrate behave differently.

PILS NO_3 versus AMS NO_3:

- AMS: significantly lower than PILS nitrate.
- Why? AMS_PM1 volatile nitrate, PILS_PM2.5 soluble nitrate
- Difference due to nitrate salts from sea-salt?

$$NaCl_{(p)} + HNO_{3(g)} \rightarrow NaNO_{3(p)} + HCl_{(g)}$$

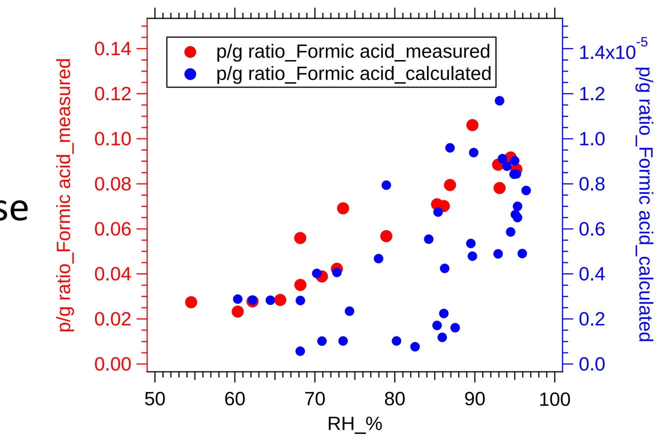




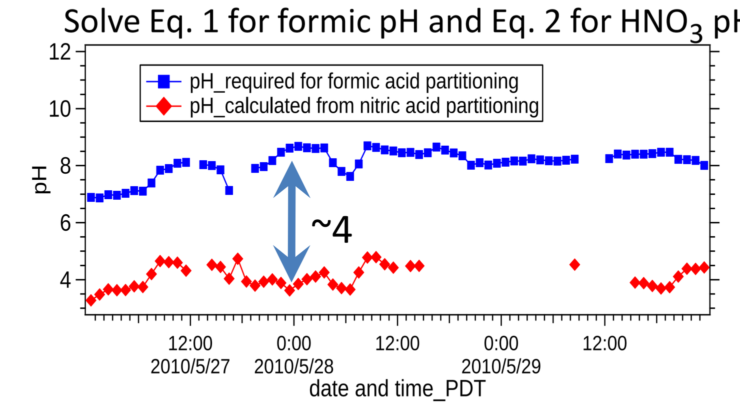
- Focus on volatile nitrate partitioning (HNO_3 and AMS_PM1 NO_3-)
- Nitric acid partitioning correlates positively with RH
- Assuming nitric acid partitioning follows thermodynamic equilibrium (Henry's Law):

$$\frac{[NO_3^-]_p}{[HNO_3]_g} = K_H * LWC * K_a * \frac{1}{[H^+]} \quad \text{Eq. 2}$$

- Solve Eq. 2 for LWC/[H+]
- Use in Eq. 1 to predict formic p/g
- Result: predicted formate concentration 4 orders of magnitude lower than measurements (~ no particle phase formate)



LWC predicted by ISORROPIA
Solve Eq. 1 for formic pH and Eq. 2 for HNO_3 pH

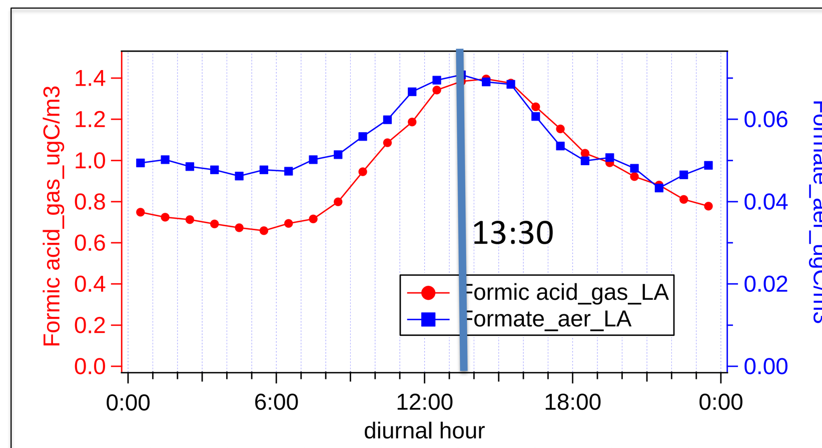


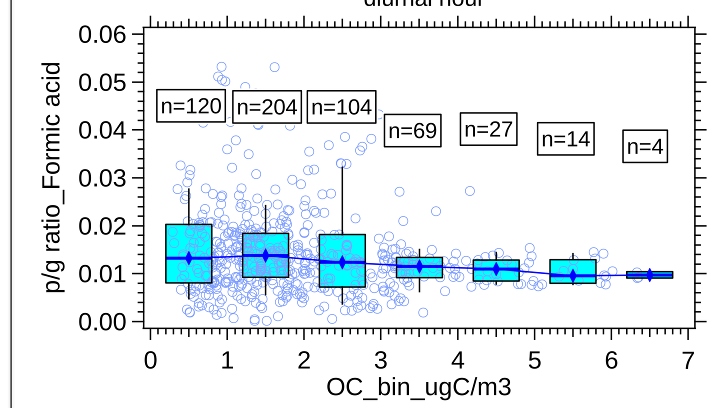
Possible reasons for difference:
- External mixture of aerosols?
- Other ongoing processes (dissolution into LWC not dominant due to low solubility)?

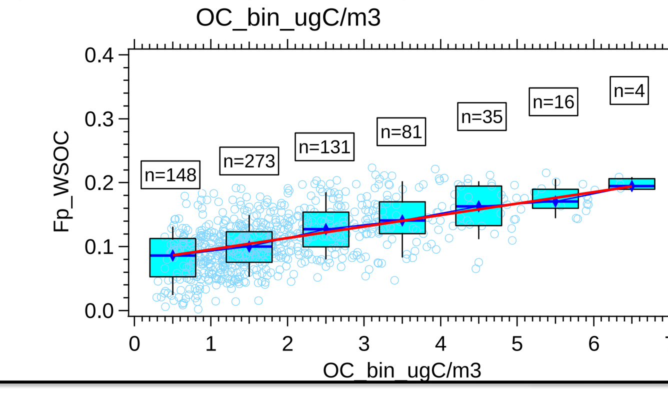
What is special about periods where partition to LWC?

- Mostly at night, some daytime periods (eg, May 27 22:30 to May 28 15:30 & June 10 12:30 to June 11 12:30) with higher than usual RH.
- Periods of low daytime photochemistry (eg, for the same times of day, HNO_3 was 1/5 of average concentration, WSOCg was 1/2), implies low production rate of gas formic acid (29% of average concentration).
- Likely multiple processes/factors influence partitioning; dissolution may dominate during these periods so most obvious

2. Formic Acid Partitioning During Dry Periods

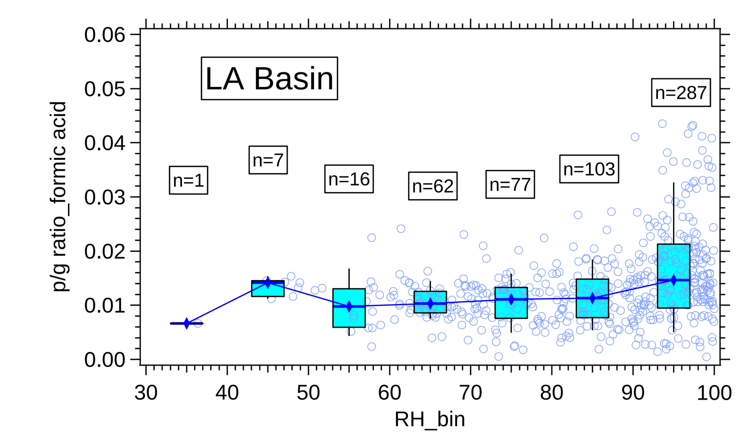


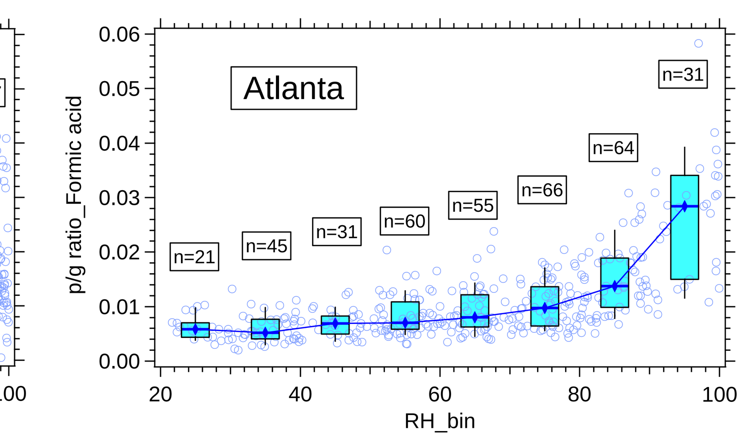




- Although partitioning under high RH is 2x that to low RH, highest particle formic acid is observed midday during period of lowest RH.
- Highest gas and particle phase concentrations occur at similar times, unlike other SVOCs and SOAs.
- Why? Large photochemical production of gas-phase formic acid, then small fraction (~1%) partitions to particle phase.
- Partitioning does not show relation to OC like WSOC does.
- What is formic partitioning to? Maybe LWC, (LWC=5 at these times vs ~ 100 ug/m3 when evidence for RH dependence (1).

Formic Acid Partitioning: LA vs. Atlanta





- In Atlanta, formic acid shows strong partitioning to liquid water, unlike LA.
- Why? Difference in VOCs (Atlanta high biogenic fraction) results in difference in formation pathways, also differences in dilution/dispersion.

Conclusions

- At the Caltech ground site formic acid partitioning (p/g) ranged between 1 and 2% with the variability related to:
  1) Partitioning to water (p/g~2%): Partitioning follows RH, but not predicted by Henry's Law based on HNO_3 partitioning: predicted pH~4, required pH~7 to 8.
  Only observed under periods of low photochemical activity indicated by low levels of SVOCs (eg, HNO_3, WSOCg). These are periods when partitioning to particle water may be most obvious amongst other processes (eg, strong gas production rates, other partitioning processes?).
  2) Partitioning when dry (p/g~1%): Highest gas and particle phase formic acid were observed during periods of intense photochemical activity (~13:00) when other SVOC concentrations highest. During this time p/g ratios about ½ those of high RH and Henry's law type partitioning is not obvious since LWC 5 vs ~ 100ug/m3 during (1).
- In contrast to LA, formic acid partitioning in Atlanta shows a clear correlation with RH throughout study period. The difference might be due to weaker formic acid photochemical production, which results from different VOC precursor concentrations due to different emission rates and/or dilution/dispersion.

Acknowledgements

This research was supported by NSF funding ATM-0931492. The authors also thank CARB for funding the site logistics and Caltech for generous assistance throughout the study.